STUDIES ON THE EXTRACTION AND ELECTROREFINING OF TIN

A Thesis

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STUDIES ON THE EXTRACTION AND ELECTROREFINING OF TIN

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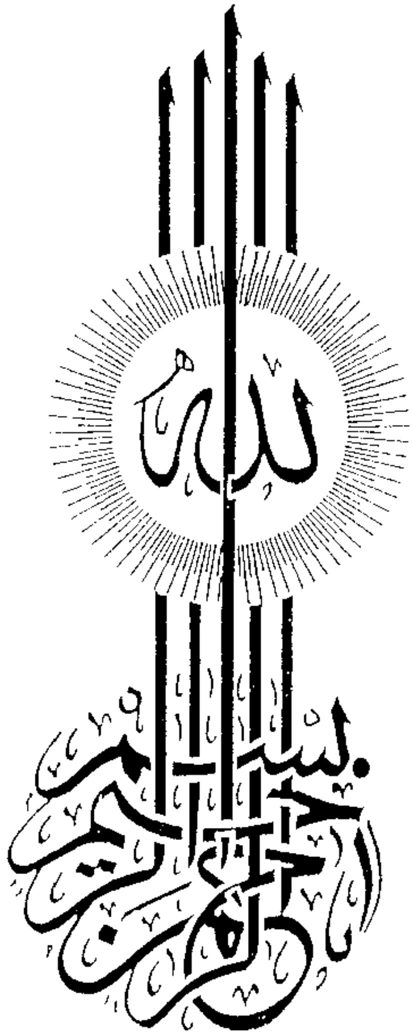
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LIST OF SYMBOLS

i	The net current density
i_c	The cathodic current
i_a	The anodic current
α_c	The cathodic transfer coefficient (that portion of the activation overpotential η, which lowers the energy barrier for deposition).
α_a	The anodic transfer coefficient
n	Number of electrons
i_o	Exchange current density
R	Ideal gas constant
T	Absolute temperature degree
F	Faraday's constant
b_c	Cathodic Tafel slope
b_a	Anodic Tafel slope
ν	Stoichiometric number
z	Order of reaction
p	Pressure
W_o	Heat of activation at open circuit
$\bar{h}$	Average surface roughness
PSA	Phenolsulphonic acid
ϕ	Cathodic current efficiency

I. HISTORICAL

Tin is one of the earliest metals known to mankind. The finding of ancient objects to which a date can be ascribed, coupled with chemical analysis of the object, is at least evidence that the material which we call tin today was used long ago.

Application of tin was fairly well known by many ancient people. The prescription in the "X" papyrus, 3rd century A.C., confirmed by Revens and Leemons[1], contained detailed instructions for making alloys with copper and silver.

Herodouts[1] wrote, about 440 B.C., of "the islands called the cassetrides, from which we are said to have our tin", and Julius Caeser four hundred years later in his report on Britain referred to the production of tin.

From earliest times tin was used for the benefit it brought on other metals rather than as a material of itself. The very early use of tin for hardening copper to get bronze was a very important step in the development of mankind. The later historians refer conveniently to a "Bronze Age" in cultural development, which has been attained at widely differing times in different parts of the world. Bronze appears to have began to displace copper in Egypt about 3000 B.C. Another ancient alloy of tin is that with lead, commonly called solder.

The extraction of tin is at least 5000 years old[2], and it can be expected that it has, by now, reached an advanced state of evolution, in which the processes arrived are close to the best.

INTRODUCTION AND AIM OF THE WORK

Tin is a soft, ductile, corrosion resistant and easily solderable element. It has a clean, attractive appearance, good plasticity, higher ability to combine with other metals to form alloys with important properties. It has the ability to retain its original appearance and is nontoxic in contact with foodstuffs. In view of these attributes, it is not surprising that tin has been used for many centuries. It has a wide field of application in the household and in industry.

Over the last few decades research and development has led to the reduction of the cost of tinned containers to meet growing competition from alternate coated steels, aluminium, glass, paper and plastics, as well as to reduce the amount of tin used because of its scarcity.

Today, the rapid growth of the electrical sectors of industry and consumer products has meant that tin and tin alloys are more important than ever. The rapid and wide adoption of semiconductor devices and the requirements in several other branches of industry and engineering physics created the demand for metal with a practically high purity in large amounts.

Tin is one of the metals needed for semiconductors; it is used in thick films which are becoming increasingly important in the modern electronics, resistors and dielectrics for use in microelectronics industries.

In Egypt, cassetrite, the main ore of tin, is distributed in different localities in the Eastern Desert of Egypt and Sinai. Among these localities are, Igla, Abu Dabbal and Nuweibi. The amounts of cassetrite present in the Eastern Desert are enough to give concentrates necessary for the production of about 40 tons per year of metallic tin covering an important part of the Egyptian annual need of this important metal.

Cassetrite concentrate from Wadi Igla was delivered by the Metallurgical Laboratories of the Egyptian Geological Survey and Mining Authority. Its analysis shows that it contains 52% tin, 7.5% Fe_2O_3 and about 15% SiO_2, beside other amounts of minor impurities.

Batches of 50 kg of this concentrate, mixed with coke, 85% fixed carbon, and silica as a flux were smelted in a submerged arc furnace in the Steel Laboratory, CMRDI. Different conditions were examined including the proportions of coke and silica added, and granulation of the reduced mixture using molasses and bentonite as binders. Smelting took place at about 1350°C, with a recovery of tin ranging from 90-95%, depending on the experimental conditions.

The crude tin produced could be refined either by a fire refining process or an electrolytic process. The main drawbacks of tin fire refining process are its multistage character, high labour expenditure and low direct recovery. On the other hand, tin electrorefining usually permits to eliminate almost all impurities in one stage, achieve a high direct extraction and avoid complex retreatment of many types of by-products.

Electrorefining of crude tin, obtained through smelting of Egyptian cassetrites, is the subject of our studies. After careful survey of the literature, it was concluded that intensive investigations are needed in order to optimise the conditions needed for the electrorefining process from both acid and alkaline baths, regarding current efficiencies and quality of the cathodic deposits obtained. The main aspects of the studies carried out include :

(1) Tin electrode-position from acid sulphate baths.

(2) The effect of the other elements present in crude tin on the electrorefining process in the acid bath.

(3) Tin electrodeposition from alkaline stannate baths.

Different factors affecting the forementioned items as the electrolyte bath compositions, temperature and current densities are investigated.

(4) The effect of organic additives, (gelatine, phenolsulphonic acid and β-naphthol), on the quality of cathodic deposits, obtained from acid baths.

(5) Kinetics of the cathodic tin deposition from acid and alkaline baths.

(6) The preconditions of anodic dissolution especially in alkaline baths are also considered.

CHAPTER I

LITERATURE SURVEY

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1.1. Electrodeposition of Tin

Electrodeposition of tin was not practiced extensively before the late 1920's. Tin exists in two valency forms and both bivalent and quadrivalent tin forms are employed in modern acid and alkaline baths.

A survey of the conditions where acid or alkaline baths were used will be presented. Generally, all the stannous baths in use today are, to some extent acidic, known as "acid baths", while stannate containing baths are often spoken of as alkaline baths.

Most of the soluble salts of these compounds had been tried both in plating and refining[3]. Sulphate, chloride, sulphamate and fluosilicate salts were considered amongst the acid baths, while the thiostannates and stannates were used in the alkaline electrolyte baths.

Many factors enter into the choice of a tin electrodeposition bath for any particular application. Generally, the alkaline baths work at higher temperatures compared with those of the acid one[3,4,5]. Sn IV ions are the current carrying species in the alkaline stannate solutions, so that the electrochemical equivalent of the acid stannous solution is double that of the alkaline stannate solutions. Thus, for a given c.d the acid bath will deposit tin twice as fast as the alkaline bath. As the cathode efficiency is usually above 95% in the acid bath, and may